FABRICATION AND CHARACTERIZATIONS OF MAGNETRON CO-SPUTTERED InAlN FILMS FOR PHOTODETECTORS APPLICATION

NAVEED AFZAL

UNIVERSITI SAINS MALAYSIA

2017

FABRICATION AND CHARACTERIZATIONS OF MAGNETRON CO-SPUTTERED InAlN FILMS FOR PHOTODETECTORS APPLICATION

by

NAVEED AFZAL

Thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy

February 2017

ACKNOWLEDGEMENT

In the name of Allah, Most Gracious, Most Merciful

All Praise is for Almighty Allah who gave me strength, inspiration and courage to complete this doctoral study.

I would like to express profound gratitude to my supervisor Dr. Mutharasu Devarajan for his creative guidance, intellectual support, stimulating discussions and inspiring words that really helped me to achieve outstanding goals in my research work. I am also grateful for his excellent hospitality, wonderful attitude and encouragement throughout my doctoral study. The friendly and yet challenging research environment he created helped me to develop and progress myself in research by leaps and bounds.

I gratefully acknowledge the financial support given by The World Academy of Sciences (TWAS) for the developing world and Universiti Sains Malaysia (USM) in the form of TWAS-USM fellowship to carry out this doctoral study.

I would like to express my great appreciation and acknowledgement to Nano-optoelectronic Research Laboratories (NOR) staff particularly, Mr. Abdul Jamil Yusuff, Mr. Anas Ahmad, Ms. Ee Bee Choo and Mr. Yushamdan Yusof for their technical support during experiments and characterizations. I also greatly appreciate the help and support provided to me by my lab mates throughout my stay here.

My heartfelt gratitude also goes to my family members: to my father and mother for their continuous prayers and support and to my sisters and my wife for their encouragement.

Naveed Afzal

February, 2017

Universiti Sains Malaysia

TABLE OF CONTENTS

ACKNOWLEDGMENT…………………………………………………………......ii

TABLE OF CONTENTS…………………………………………………….....iii

LIST OF TABLES…………………………………………………….............x

LIST OF FIGURES……………………………………………………………...xi

LIST OF SYMBOLS…………………………………………………….........xv

LIST OF ABBREVIATION…………………………………………….............xvii

ABSTRAK………………………………………………………...................xix

ABSTRACT……………………………………………………….................xxi

CHAPTER 1: INTRODUCTION…………...1

1.1 Introduction to III-V Nitrides……………………………………….....1

1.2 Introduction to InAlN………………………………………………......3

1.3 Problem Statement………………………………………………….......5

1.4 Objectives of Research…………………………………………….........7

1.5 Scope of Study…………………………………………………………....7

1.6 Originality of Thesis………………………………………………….......8

1.7 Organization of Thesis …………………………………………………....8

CHAPTER 2: LITERATURE REVIEW AND THEORY………………….........11

2.1 Introduction……………………………………………………………........11

2.2 Overview of InN Growth…………………………………………………....11

2.3 Overview of AlN Growth…………………………………………….......13

2.4 Fundamental Properties of InN and AlN……………………………….....14

2.5 Overview of InAlN Growth…………………………………………........16

2.5.1 Growth Techniques……………………………………………………...17
2.5.1(a) Metalorganic Chemical Vapor Deposition……………......17
2.5.1(b) Molecular Beam Epitaxy…………………………….........20
2.5.1(c) Reactive Magnetron Sputtering…………………….........21
2.6 Physical Properties of InAlN……………………………………….......24
2.6.1 Structural Properties……………………………………….........24
2.6.2 Optical Properties…………………………………………….......26
2.6.3 Electrical Properties……………………………………….......28
2.7 Applications of InAlN……………………………………………..........30
2.8 Theory of Sputter Deposition………………………………………..........32
2.8.1 Principle of Sputter Deposition……………………………..........33
2.8.2 Types of Sputtering……………………………………………........33
2.8.2(a) Direct Current Sputtering………………………….........34
2.8.2(b) Radiofrequency Sputtering………………………….......34
2.8.2(c) Magnetron Sputtering………………………………..........35
2.8.2(d) Reactive Sputtering…………………………………..........35
2.8.3 Sputtering Parameters……………………………………............35
2.9 Fundamentals of X-ray Diffraction…………………………………..........36
2.10 Field Emission Scanning Electron Microscopy…………………….........38
2.11 Energy Dispersive X-ray Spectroscopy……………………………..........40
2.12 Atomic Force Microscopy……………………………………………..........40
2.13 UV-Vis Spectroscopy……………………………………………………......41
2.14 Hall Effect Theory………………………………………………………......43
2.15 Metal-Semiconductor Contacts……………………………………….......45
2.15.1 Ohmic and Schottky Contacts…………………………………..........45

2.15.2 Thermionic Emission Theory…………………………………….....47

2.16 Metal-Semiconductor-Metal Photodetector……………………………........48

CHAPTER 3: EXPERIMENTAL PROCEDURE…………………………........50

3.1 Introduction………………………………………………………………....50

3.2 Preparations of Substrates……………………………………………….....50

3.2.1 Substrates Cutting…………………………………………………......51

3.2.2 Substrates Cleaning…………………………………………….........51

3.2.2(a) Silicon Substrates……………………………………….....51

3.2.2(b) Gallium Arsenide Substrates………………………….........52

3.2.2(c) Sapphire and Glass Substrates…………………………......52

3.3 Deposition of InAlN Films………………………………………………....52

3.3.1 Deposition of InAlN Films on Si (111) Substrates……………........54

3.3.2 Deposition of InAlN Films on Different Substrates………………..57

3.3.3 Deposition of InAlN Films on GaAs Substrates……………….........58

3.3.4 Deposition of InAlN on Si (111) with Optimized Conditions……...59

3.4 Metal Contact Deposition…………………………………………………......60

3.5 Characterization Techniques…………………………………………….......60

3.5.1 X-ray Diffraction Analysis………………………………….........60

3.5.2 Surface Characterizations…………………………………………..61

3.5.3 Elemental Analysis……………………………………………….....61

3.5.4 Band gap Analysis……………………………………………….........61

3.5.5 Hall Effect Measurements…………………………………….......62

3.5.6 Current-Voltage Measurements……………………………..........62

3.6 Device Fabrication and Characterization…………………………………...63

CHAPTER 4: RESULTS AND DISCUSSION…………………………………......65

GROWTH OF InAlN FILMS ON Si (111) SUBSTRATES BY REACTIVE MAGNETRON CO-SPUTTERING

4.1 Introduction……………………………………………………………......65

4.2 Growth and Characterizations of $In_xAl_{1-x}N$ films at Different Indium Mole Fractions………………………………………………………………........65

4.2.1 Structural Characterization…………………………………........66

4.2.2 Surface Characterizations…………………………………..........69

4.2.2(a) Surface Morphology………………………………........69

4.2.2(b) Surface Roughness Analysis……………………….........73

4.2.3 Elemental Analysis…………………………………………......75

4.2.4 Electrical Characterizations…………………………………......75

4.2.4(a) Hall Measurements……………………………………...76

4.2.4(b) Current-Voltage Characteristics…………………............77

4.2.5 Band Gap Analysis……………….…………………………........78

4.3 Growth and Characterizations of InAlN Films at Different Substrate Temperature……………………………………………………………........81

4.3.1 Structural Characterization……………………………………......81

4.3.2 Surface Characterizations……………………………………......84

4.3.2(a) Surface Morphology……………………………………...84

4.3.2(b) Surface Roughness Analysis…………………………......86

4.3.3 Elemental Analysis………………………………………….......87

4.3.4 Electrical Characterizations……………………………….......88

4.3.4(a) Hall Measurements…………………………………......88

4.3.4(b) Current-Voltage Characteristics……………………........91

4.4 Growth and Characterizations of InAlN Films at Different Thicknesses......91

4.4.1 Film Thickness Measurement……………………………….......91

4.4.2 Structural Characterization…………………………………….......92

4.4.3 Surface Characterizations……………………………………........96

4.4.3(a) Surface Morphology…………………………….............96

4.4.3(b) Surface Roughness Analysis………………………….... 98

4.4.4 Elemental Analysis……………………………………………100

4.4.5 Electrical Characterizations……………………………………...100

4.4.5(a) Hall Measurements…..…………………………………101

4.4.5(b) Current-Voltage Characteristic….……………………...104

4.5 Growth and Characterizations of InAlN Films at Different Ar:N_2……….....105
Gas Flow Ratios

4.5.1 Structural Characterization………………………………….....105

4.5.2 Surface Characterizations…………………………………......108

4.5.2(a) Surface Morphology…………………………………......108

4.5.2(b) Surface Roughness Analysis……………………….....110

4.5.3 Elemental Analysis……………………….................................112

4.5.4 Electrical Characterizations………………………………........113

4.5.4(a) Hall Measurements……………………………........113

4.5.4(b) Current-Voltage Characteristics………………….........114

4.6 Optimized Deposition Parameters...116

CHAPTER 5: RESULTS AND DISCUSSION……………………………......117

GROWTH OF InAlN FILMS ON DIFFERENT SUBSTRATES BY REACTIVE MAGNETRON CO-SPUTTERING

5.1 Introduction………………………………………………………...117

5.2 A Comparative Study on the Growth of InAlN Films on………………....117
Different Substrates

5.2.1 Structural Characterization….…………………………………...118

5.2.2 Surface Characterizations……………………………………...123

5.2.2(a) Surface Morphology……………………………………..123

5.2.2(b) Surface Roughness Analysis……………………….........126

5.2.3 Electrical Characterizations……………………………………....127

5.2.4 Band Gap Analysis…………………………………………….....130

5.3 Growth and Characterizations of InAlN Films on GaAs Substrates......…..132

5.3.1 Structural Characterization……………………………….........132

5.3.2 Surface Morphology……………………………………….......135

5.3.3 Electrical Characterizations……………………………………....136

5.3.3(a) Hall Measurements……………………………………....136

5.3.3(b) Current-Voltage Characteristics……………………….......137

5.3.4 Band Gap Analysis…………………………………………….....139

CHAPTER 6: RESULTS AND DISCUSSION………………………………...141

CHARACTERIZATION OF InAlN BASED PHOTODETECTORS

6.1 Introduction…………………………………………………….........141

6.2 Characterizations of InAlN/Si (111) based MSM Photodetector……….......141

6.2.1 Characterizations of InAlN Film Grown on Si (111)…………........142

6.2.1(a) Structural Characterization……………………………......142

6.2.1(b) Surface Characterizations………………………….........143

6.2.1(c) Band Gap Analysis/Hall Measurements..…………….......144

6.3 InAlN based MSM Photodetector……………………………………....145

6.3.1 Responsivity…………………………………………………......145

6.3.2 Current-Voltage Characteristics……………………………….......146

6.3.3 Sensitivity and Current Gain……………………………………....148

6.3.4 Response and Recovery Time……………………………….......150

6.4 Characterization of n-InAlN/p-Si (111) Heterojunction Photodiode…........151

6.4.1 Responsivity…………………………………………………………......151

6.4.2 Current-Voltage Measurements…………………………………….....152

6.4.3 Sensitivity and Current Gain……………………………………......153

6.4.4 Response and Recovery Time……………………………………......154

6.5 Characterizations of InAlN/GaAs based MSM Photodetector……............157

6.5.1 Responsivity…………………………………………………….........157

6.5.1 Current-Voltage Measurements………………………………........158

6.5.3 Sensitivity and Current Gain…………………………………........159

6.5.4 Response and Recovery Time……………………………………......161

CHAPTER 7: CONCLUSIONS AND FUTURE WORKS……………............162

7.1 Conclusions………………………………………………………...........162

7.2 Future Works…………………………………………………................164

REFERENCES

LIST OF PUBLICATIONS

LIST OF TABLES

		Page
Table 2.1	Electron concentration in $In_xAl_{1-x}N$ films grown on different substrates	29
Table 2.2	Photodetection parameters of various types of photodetectors	32
Table 3.1	Deposition parameters of InAlN films synthesized on Si (111)	56
Table 3.2	Deposition parameters of InAlN films grown on different substrates	57
Table 3.3	Deposition parameters of InAlN films grown on GaAs substrates	58
Table 3.4	Deposition parameters of InAlN films with optimized conditions	59
Table 4.1	Variations in structural parameters with In mole fraction x	69
Table 4.2	Elemental composition of $In_xAl_{1-x}N$ at different In mole fractions	75
Table 4.3	Electron concentration and mobility of $In_xAl_{1-x}N$ films	77
Table 4.4	Variations in structural parameters of InAlN with deposition temperature	83
Table 4.5	Elemental composition of InAlN at different temperatures	88
Table 4.6	Variations in structural parameters with film thickness	95
Table 4.7	Elemental composition of InAlN at different thicknesses	100
Table 4.8	Variations in electrical parameters of InAlN with film thickness	102
Table 4.9	Structural parameters of InAlN at different Ar:N_2 gas flow ratio	107
Table 4.10	Elemental composition of InAlN at different Ar:N_2 gas flow ratio	112
Table 4.11	Variation in electrical parameters of InAlN with Ar:N_2 ratio	114
Table 4.12	List of optimized deposition parameters of InAlN on Si (111)	116
Table 5.1	Structural parameters of InAlN films prepared on GaAs (100)	134
Table 5.2	Electrical parameters of InAlN films prepared on GaAs (100)	137

LIST OF FIGURES

		Page
Figure 1.1	Band gap energy vs lattice constant of III-Nitride semiconductors at room temperature	2
Figure 2.1	Reflection spectra of $In_{1-x}Al_xN$ films on sapphire substrates	27
Figure 2.2	Schematic diagram of sputtering process	33
Figure 2.3	(a) Schematic diagram of X-ray diffractometer (b) Principle of XRD	38
Figure 2.4	Schematic diagram of FESEM	39
Figure 2.5	Schematic diagram of AFM	40
Figure 2.6	Schematic diagram of UV-Vis spectrometer	42
Figure 2.7	Schematic diagram of Hall Effect	43
Figure 2.8	Schematic diagram of metal-semiconductor contact	46
Figure 3.1	Magnetron sputtering deposition system (a) Magnetron sputtering system (b) Sputtering chamber (c) Metal targets	53
Figure 3.2	(a) Schematic diagram of Al metal contacts for Hall measurement	62
Figure 3.3	Schematic diagram of Pt metal contacts for MSM photodetector fabrication	63
Figure 3.4	Set-up for the I-V measurements of photodetectors	64
Figure 4.1	XRD patterns of $In_xAl_{1-x}N$ films on Si (111) substrate	67
Figure 4.2	Surface morphology of $In_xAl_{1-x}N$ films (a) x = 0.25 (b) x=0.72 (c) x=0.86 (d) x= 1	70
Figure 4.3	Schematic diagram of thin film growth process	71
Figure 4.4	AFM images of $In_xAl_{1-x}N$ films (a) x = 0.25 (b) x=0.72 (c) x=0.86 (d) x= 1 (e) Variation in surface roughness with changes in In mole fraction	74
Figure 4.5	Variations in electrical resistivity of $In_xAl_{1-x}N$ films with In composition x	77

Figure 4.6	I-V characteristics of $In_xAl_{1-x}N$ films	78
Figure 4.7	(a) UV-Vis reflectance spectra of $In_xAl_{1-x}N$ films (b) Bang gap of $In_xAl_{1-x}N$ films as function of x	80
Figure 4.8	XRD patterns of InAlN films at various temperatures	83
Figure 4.9	Surface morphology of InAlN films at different substrate temperatures	85
Figure 4.10	AFM images of InAlN films at different temperatures (a) RT (b) 100 ^oC (c) 200 ^oC (d) 300 ^oC	86
Figure 4.11	Variations in surface roughness with substrate temperatures	87
Figure 4.12	(a) Variations in electron concentration with substrate temperatures (b) Variations in electrical resistivity with substrate temperatures (c) Current-voltage characteristics of InAlN films at different substrate temperatures	90
Figure 4.13	Cross-sectional images of InAlN films	92
Figure 4.14	XRD patterns of InAlN films at different thicknesses	93
Figure 4.15	Surface Morphology of InAlN films grown at different thicknesses (a) 150 nm (b) 250 nm (c) 380 nm (d) 750 nm (e) 1050 nm (f) Grain size as a function of InAlN film thickness	97
Figure 4.16	AFM images of InAlN films (a) 150 nm (b) 250 nm (c) 380 nm (d) 750 nm (e) 1050 nm, (f) Variations in RMS surface roughness with change of film thickness	99
Figure 4.17	Variations of electrical resistivity of InAlN with changing film thickness	101
Figure 4.18	I-V characteristics of InAlN films at different film thicknesses	104
Figure 4.19	XRD patterns of InAlN films on Si (111) substrates at different gas flow ratios	106
Figure 4.20	Surface morphology of InAlN films at different Ar:N_2 gas flow ratios	109
Figure 4.21	Variations in grain size with change of Ar:N_2 gas flow ratio	110

Figure 4.22	(a-d) AFM images of InAlN films at different Ar:N_2 ratio (e) Variation of RMS surface roughness with gas flow ratio	111
Figure 4.23	Variations in electrical resistivity of InAlN with change of Ar:N_2 gas flow ratio	113
Figure 4.24	Current-voltage graphs of InAlN films at different Ar:N_2 gas flow ratio	115
Figure 5.1	XRD patterns of InAlN films grown on different substrates at 300 ^oC	119
Figure 5.2	Variations in structural parameters of InAlN films grown on different substrates	120
Figure 5.3	FESEM micrographs of InAlN films grown on different substrates	123
Figure 5.4	Grain size variations of In-rich InAlN film on different substrates	124
Figure 5.5	(a-d) AFM images of InAlN films grown on different substrates (e) Comparison of surface roughness of InAlN on different substrates	127
Figure 5.6	(a) Variation in resistivity with change of substrate (b) Variation in carrier concentration with change of substrate (c) Variation in mobility with change of substrate	128
Figure 5.7	(a) UV-Vis reflectance spectra of InAlN films grown on Si and GaAs (b) Tauc Plot of InAlN absorption spectra obtained on glass and sapphire	131
Figure 5.8	XRD patterns of InAlN films prepared on GaAs substrates at different Al powers	133
Figure 5.9	Surface morphology of InAlN films grown on GaAs substrates at different Al power	136
Figure 5.10	I-V characteristics of $In_{1-x}Al_xN$ films grown on GaAs substrates at various Al powers	138
Figure 5.11	UV-Vis reflectance spectra of InAlN films at different Al powers	140
Figure 5.12	Variations in band gap of InAlN films with Al power	140
Figure 6.1	XRD pattern of InAlN film grown on Si (111) substrate	142

Figure 6.2	(a) Surface morphology of InAlN film (b) AFM image of InAlN film	143
Figure 6.3	UV-Vis reflectance spectrum of InAlN film	144
Figure 6.4	Responsivity of MSM photodetector as function of wavelength	146
Figure 6.5	I-V characteristics of InAlN based MSM photodetector	147
Figure 6.6	(a-e) Current-time pulses of InAlN based MSM photodetector (f) Variations in sensitivity with bias voltage	149
Figure 6.7	(a) Rise and (b) fall of current-time pulses of InAlN film based MSM photodetector	150
Figure 6.8	Responsivity of n-InAlN/p-Si (111) as function of wavelength	151
Figure 6.9	I-V characteristics of n-InAlN/p-Si (111) photodiode	153
Figure 6.10	Current-time pulses of n-InAlN/p-Si (111) photodiode	155
Figure 6.11	Variations in (a) current gain and (b) sensitivity of n-InAlN/p-Si (111) photodiode with bias voltage	156
Figure 6.12	(a) Rise and (b) fall of current-time pulses of n-InAlN/p-Si(111) photodiode	156
Figure 6.13	Responsivity of InAlN/GaAs MSM UV photodetector as function of wavelength	158
Figure 6.14	I-V characteristics of InAlN/GaAs based MSM photodetector	159
Figure 6.15	(a-c) Current-time pulses of InAlN/GaAs MSM UV photodetector (e) Variation in sensitivity with bias voltage	160
Figure 6.16	(a) Rise and (b) fall of current-time pulses of InAlN/GaAs MSM UV photodetector	161

LIST OF SYMBOLS

T	Absolute temperature
Al	Aluminum
Å	Angstrom
A	Area
d	Atomic spacing
E_g	Band gap energy
k_B	Boltzmann constant
n_c	Carriers concentration
D	Crystallite Size
I	Current
a	Cubic lattice constant
I_d	Dark current
θ	Diffraction angle
η	Efficiency
χ_s	Electron affinity
q	Electronic charge
n_e	Electron concentration
σ	Electrical conductivity
μ_e	Electron mobility
ρ	Electrical resistivity
E_F	Fermi level
B	Full width at half maximum
G	Gain
V_H	Hall voltage

c	Hexagonal lattice constant
n	Ideality factor
In	Indium
P_{in}	Input power
ϕ_m	Metal work function
I_P	Photocurrent
h	Planck’s constant
R	Responsivity
A^*	Richardson co-efficient
I_s	Saturation current
Φ_{SB}	Schottky barrier height
Φ_S	Semiconductor work function
S	Sensitivity
Si	Silicon
ε	Strain
V	Voltage
λ	Wavelength

LIST OF ABBREVIATIONS

AC	Alternating current
a.u.	Arbitrary unit
AFM	Atomic force microscope
BR	Bragg reflectors
CVD	Chemical vapor deposition
C_B	Conduction band
I-V	Current-Voltage
DC	Direct current
eV	Electron volt
EDS	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscope
FWHM	Full width at half maximum
HEMT	High electron mobility transistor
K.E.	Kinetic energy
LM	Lattice mismatch
LED	Light emitting diode
M	Metal
MOCVD	Metal organic chemical vapor deposition
MS	Metal-Semiconductor
MSM	Metal-semiconductor-metal
MBE	Molecular beam epitaxy
PD	Photodiode
PL	Photoluminescence
PVD	Physical vapor deposition
Pt	Platinum

RF	Radiofrequency
RMS	Root mean square
RT	Room temperature
SBH	Schottky barrier height
Sccm	Standard cubic centimeters per min
UV	Ultraviolet
Vis	Visible
XRD	X-ray diffraction

FABRIKASI DAN PENCIRIAN FILEM InAlN PERCIKAN BERSAMA MAGNETRON BAGI APLIKASI PENDERIA FOTO

ABSTRAK

Dalam kajian ini, pertumbuhan filem indium aluminium nitrida (InAlN) telah dikaji pada substrat yang berbeza dengan menggunakan teknik percikan bersama magnetron reaktif. Kajian ini tertumpu kepada pertumbuhan filem InAlN kaya-In di atas substrat jenis-p Si (111) dengan sifat fizikal yang lebih baik. Sifat struktur InAlN disiasat melalui analisis belauan sinar-x (XRD). Sifat permukaan telah dikaji melalui mikroskop imbasan elektron (FESEM) dan mikroskop daya (AFM), manakala sifat elektrik dikaji dengan teliti melalui ukuran Hall dan ciri arus-voltan (I-V) filem. Jurang jalur telah dianggar melalui spektroskopi pemantulan UV-Vis. Kajian ini telah dibahagikan kepada tiga bahagian utama. Dalam bahagian pertama, sifat pertumbuhan dan sifat filem InAlN yang difabrikasi melalui teknik percikan bersama magnetron telah dikaji secara menyeluruh pada permukaan substrat Si (111) dari segi variasi dalam komposisi filem, suhu substrat, ketebalan filem dan nisbah aliran gas. Filem InAlN telah didepositkan pada substrat jenis-p Si (111) melalui teknik percikan bersama magnetron reaktif dengan menggunakan sasaran In dan Al dalam atmosfera Ar-N_2 dalam keadaan pemendapan yang berbeza. Keputusan XRD menunjukkan bahawa kualiti struktur filem telah dipertingkatkan dengan meningkatkan pecahan mol x In dalam $In_xAl_{1-x}N$ daripada 0.25 kepada 0.86. Kerintangan elektrik dan jurang jalur filem telah menurun dengan peningkatan nilai x. Pertumbuhan filem InAlN kaya-In juga dikaji pada suhu substrat yang berbeza dalam julat suhu bermula dari suhu bilik hingga 300 °C. Analisis struktur mendedahkan peningkatan dalam keamatan puncak pembelauan InAlN yang berorientasikan paksi-c dengan peningkatan pada suhu substrat. Ciri permukaan

menggambarkan peningkatan dalam saiz zarah dan kekasaran permukaan. Manakala kajian dari segi sifat elektik menunjukan penurunan dalam kerintangan elektrik filem dengan peningkatan pada suhu substrat. Di samping itu, dengan mengubah ketebalan filem daripada 150 kepada 1050 nm, kualiti kristal bertambah baik tetapi pilihan orientasi filem telah berubah daripada (002) kepada (101) pada ketebalan 1050 nm. Tambahan pula, dengan menyelaraskan nisbah gas Ar:N_2 pada 12:8, sifat struktur, sifat permukaan dan juga sifat elektrik filem telah dipertingkatkan. Dalam bahagian kedua tesis ini, pertumbuhan InAlN kaya-In telah dikaji pada substrat yang berbeza. Kajian perbandingan pertumbuhan filem pada permukaan substrat Si (111), nilam, n-GaAs (100) dan kaca telah dijalankan. Didapati bahawa, sifat struktur InAlN adalah lebih baik pada substrat Si (111) dan nilam berbanding substrat n-GaAs dan kaca.Tambahan pula, pertumbuhan filem InAlN juga dikaji pada substrat ZnO/GaAs (100) dengan kuasa percikan Al yang berbeza. Dalam bahagian ketiga, iaitu bahagian terakhir tesis ini, InAlN berasaskan logam-semikonduktor-logam (LSL) dan alat pengesan cahaya heterojunction telah dikaji. Tiga jenis alat pengesan cahaya yang berbeza telah direka dan cirinya termasuklah alat pengesan cahaya tampak InAlN/Si (111) LSL, fotodiode cahaya tampak heterojunction n-InAlN/p-Si (111) dan alat pengesan cahaya InAlN/GaAs (100) LSL UV. Fabrikasi peranti telah menunjukkan kepekaan dan tindak balas yang tinggi dalam keadaan yang diterangi cahaya.

FABRICATION AND CHARACTERIZATIONS OF MAGNETRON CO-SPUTTERED InAlN FILMS FOR PHOTODETECTORS APPLICATION

ABSTRACT

In this work, growth of indium aluminum nitride (InAlN) film was studied on different substrates by using reactive magnetron co-sputtering technique. The study was mainly focused to grow In-rich InAlN film on p-type Si (111) substrate with improved physical properties. The structural properties of InAlN were investigated through X-ray diffraction (XRD) analysis, surface properties were studied through field emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM) whereas the electrical properties were examined by taking Hall measurements and current-voltage (I-V) characteristics of the films. The band gap of InAlN was estimated through UV-Vis reflectance spectroscopy. The work was divided into three major parts. In the first part, growth and properties of magnetron sputtered InAlN films were comprehensively studied on Si (111) substrates by changing the film composition, substrate temperature, film thickness and gas flow ratio. The InAlN film was deposited on p-type Si (111) substrates by using reactive magnetron co-sputtering of pure In and Al targets in Ar-N_2 atmosphere under different deposition conditions. The XRD results indicated that by increasing In mole fraction x in $In_xAl_{1-x}N$ from 0.25 to 0.86, its structural quality is improved. The electrical resistivity and band gap of the film were decreased with increase of the x value. The growth of In-rich InAlN film was also studied at different substrate temperatures ranging from room temperature to 300 ^oC. The structural analysis revealed an increase in the intensity of c-axis oriented InAlN diffraction peak with increase of the substrate temperature. The surface characterization depicted an increase of grain size and surface roughness whereas the electrical studies showed a

decrease in electrical resistivity of the film with increase of the substrate temperature. By varying the film thickness from 150 nm to 1050 nm thickness, its crystalline quality was improved, however, the preferred orientation of the film was changed from (002) to (101) at 1050 nm. Similarly, by adjusting the Ar:N_2 gas ratio to 12:8, the structural, surface and electrical properties of the film were improved. In the second portion of this thesis, growth of In-rich InAlN was studied on different substrates. A comparative study of the film's growth on p-Si (111), sapphire, n-GaAs (100) and glass substrates displayed better structural properties of InAlN on Si (111) and sapphire as compared to the other substrates. In addition to this, growth of InAlN film was also investigated on ZnO/GaAs (100) substrates at different Al sputtering powers. In the third and final section of this thesis, InAlN based metal-semiconductor-metal (MSM) and heterojunction photodetectors were characterized. Three different types of photodetectors were fabricated and characterized which include InAlN/Si (111) MSM visible photodetector, n-InAlN/p-Si (111) heterojunction visible photodiode and InAlN/GaAs(100) MSM UV photodetector. The fabricated devices showed high sensitivity and responsivity under the illuminated conditions.

CHAPTER 1

INTRODUCTION

1.1 Introduction to III-V Nitrides

Interest in the growth of group III-V nitrides has been increased enormously during the last couple of decades because of their direct band gap, outstanding electrical and optical properties which make them suitable for applications in optoelectronics and high power electronic devices. A III-V nitride semiconductor is formed when group-III element such as, indium (In), aluminum (Al), gallium (Ga) or boron (B) is bonded with the nitrogen which is the group-V element. The commonly used III-V nitrides include InN, GaN and AlN and their alloys. The advancements in the field of III-V nitrides have been remarkable in recent years. The III-V nitride materials find promising applications in light emitting diodes, photodiodes, solar cells, high mobility electron transistors and sensors. Among the group of III-V nitrides, the InN possesses a narrow band gap, smallest effective mass, high electron mobility and high drift velocity. The energy band gap value of InN is found to be 0.7 eV at room temperature and therefore InN has potential applications in solar cells and high frequency electronic devices [1-3]. On the other hand, the AlN possesses a wide band gap of 6.2 eV and it has good thermal conductivity, high stability and hardness at high temperatures. Therefore, it is widely used in electronic packaging and for piezoelectric applications [4-6]. GaN is also a wide band gap material having energy band gap of 3.4 eV. GaN and its alloys with InN and AlN are widely used for optoelectronic applications such as in light emitting diodes [7-9].

It is possible to modify the band gap of a device from 0.7 eV to 6.2 eV through alloying of InN, GaN and AlN with each other. When InN is alloyed with

GaN, band gap of the resultant material can be varied from 0.7 eV to 3.4 eV [10]. When InN is alloyed with AlN, the band gap of resultant nitride can be altered from 0.7 eV to 6.2 eV by controlling the composition of the alloy [11-12]. However, solubility of the III-V nitrides has been one of the major issues in obtaining high quality nitride alloys. The band gaps and lattice constants of III-V nitrides are shown in Figure 1.1. As seen from the figure, there exists a large difference in the band gaps and lattice constants of InN, GaN and AlN. Therefore, it has been difficult to fabricate III-V nitride alloys with high structural quality in the past. In the case of AlGaN and InGaN, a considerable success has been achieved in a whole composition range [13-14], however, the growth of InAlN has been limited due to difficulties associated with it. This is mainly due to a large difference between the lattice parameters of InN and AlN that creates problems in their solubility [12].

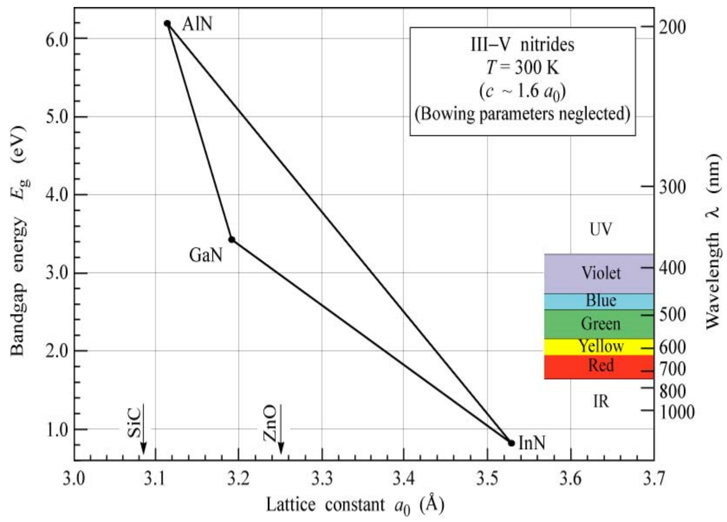

Figure 1.1 Band gap energy vs lattice constant of III-Nitride semiconductors at room temperature [15]

The III-V nitrides can mainly crystallize into three different types of crystal structures named as wurtzite (hexagonal), zinc-blende (cubic) and rocksalt structures. The wurtzite structure is thermodynamically stable under ambient conditions whereas the zinc-blende is a metastable structure. A phase transition to rocksalt structure takes place at high pressure. The wurtzite structure has hexagonal unit cell having lattice constants a and c whereas, the zinc-blende structure is formed from a group of cubic unit cells having same lattice constants in all three perpendicular directions [16]. The wurtzite structure differs from the zinc-blende cubic structure in its orientation and stacking order. The stacking order for (0001) plane in wurtzite crystal is ABABAB in <0001> direction whereas for the zinc-blende crystal, the stacking sequence of (111) plane is ABCABCABC along <111> orientation. Due to these similarities, the zinc-blende crystal structure is often found in the bulk of wurtzite crystals due to the presence of stacking faults in the material [17-18]. The zinc-blende structure can also be obtained when the nitride film is grown on a cubic substrate; however, quality of the zinc-blende III-V nitrides is not as good as that of the wurtzite III-V nitrides. Therefore, III-V nitrides devices are mostly constructed based on their wurtzite structure. The III-V nitrides find useful applications in optoelectronics and in RF power electronics. The use of III-V nitrides for these applications depends upon their fundamental properties. The III-V nitrides with direct and large band gap are considered to be suitable for the optoelectronic applications. The use of these nitrides allows the fabrication of efficient photon emitters and detectors across the visible and ultraviolet spectra. In the case of RF power electronics, III-V nitrides with high electron velocity, high break down field, low intrinsic carrier concentration and high thermal conductivity are preferred [18-19].

1.2 Inroduction to InAlN

Indium aluminum nitride (InAlN) is a ternary III-V nitride which has gained a tremendous attention of researchers in recent times because of its remarkable properties and potential applications in the electronic and optoelectronic industries. The InAlN is formed when InN and AlN are alloyed with each other, therefore, properties of InAlN depend upon the properties of its binary constituents i.e. InN and AlN. Among the III-V nitrides, InAlN is one such nitride that shows the widest band gap variations as compared to the other III-V nitrides. The band gaps of InN and AlN are found to be ~ 0.7 eV and 6.2 eV respectively at room temperature, therefore the band gap of InAlN can be adjusted between 0.7 eV and 6.2 eV by adjusting the mole fractions of In and Al in it [20]. InAlN films possess potential applications in light emitting diodes, solar cells, transistors, laser diodes, photodiodes, sensors and Bragg reflectors [21-23]. A cladding layer of InAlN on GaN is found to be strain free because of near lattice matching of InAlN with GaN and it is preferred over InGaN for the optoelectronic applications [24]. However, despite the remarkable properties and potential applications of InAlN alloys in the optical and electronic industry, its growth has been quite difficult and challenging because of the large differences present in the physical and chemical parameters of InN and AlN. The difference of covalent bonds, ionic sizes, lattice constants, thermal stabilities and growth temperatures creates difficulty in the solubility between InN and AlN. The lattice mismatch between AlN (3.112 Å) and InN (3.545 Å) has been found to be quite large [12]. There exist a difference in the bonding energies of AlN (2.88 eV) and InN (1.98 eV) [15] and thus InN growth takes place at low temperature whereas the AlN requires higher temperature for its preparation. These differences may cause phase separation and compositional inhomogeneities in InAlN films [25].

Various growth techniques such as metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE) and magnetron sputtering have been employed to synthesize InAlN films on different substrates [25-28]. However, the crystalline quality of InAlN alloys has not been as good as that of the other III-V nitrides. Therefore, efforts are in progress in recent times to improve the structural, optical and electronic properties of InAlN alloys.

1.3 Problem Statement

InAlN is in great demand in semiconductor industry because of its novel properties and remarkable applications in the electronic and optoelectronic devices. Improvement in the structural quality of InAlN alloy has been a major issue due to a huge immiscibility gap between the properties of its binary constituent elements i.e. InN and AlN. Therefore, InAlN has received a limited attention in the past as compared to the other III-V nitrides such as InN, GaN, AlGaN and InGaN etc. InAlN films growth using conventional epitaxial techniques such as the MOCVD and MBE suffers from difficulties because of the differences in growth temperatures of InN and AlN. The preparation of InN requires low temperature (600 ^{o}C) whereas the AlN growth takes place at higher temperature (1100 ^{o}C) by using epitaxial techniques which makes it hard to prepare InAlN alloys with appropriate composition due to thermal decomposition of InN at higher temperatures [29]. As a result, the MOCVD and MBE growth of InAlN films is often accompanied by phase separation in the films [30]. Therefore, despite the intensive research, many of the fundamental properties of pure InAlN alloys are still remain unclear.

The choice of a suitable substrate has also been a major issue in the growth of InAlN films. The non-availability of a suitable substrate creates a huge difficulty in the growth of high quality InAlN alloy. Although some success has been achieved in the growth of Al-rich InAlN alloys on GaN/sapphire substrates due to near lattice matching between $In_{0.17}Al_{0.83}N$ and GaN, however, on the In-rich side only few studies have been reported [31]. The main reason is the lack of a suitable substrate for the preparation of In-rich InAlN layers due to deterioration of the film's quality at high temperatures.

In this work, the reactive magnetron co-sputtering technique has been used to grow InAlN alloys. The advantage of this technique is that it is relatively a low cost and low temperature growth technique as compared to the MOCVD and MBE. The films deposited using this technique show good adhesion to the substrate with high mechanical integrity and stability which depends upon the growth parameters [32]. Moreover, the problems of phase separation in InAlN film grown by using magnetron sputtering technique are avoided because of its relatively lower growth temperature as compared to MOCVD and MBE techniques. The survey of literature reveals that only a limited number studies have been carried out to grow InAlN alloys using reactive magnetron sputtering technique. In this work, a particular attention has been given to grow InAlN film on Si (111) substrate that offers the lowest lattice mismatch as compared to the other substrates for the growth of In-rich InAlN film. In addition to this, growth of InAlN films has been studied on GaAs (100) substrate at different compositions. GaAs is considered to be a valuable and desirable substrate for the manufacturing of optoelectronic devices because of its direct band gap, high electron mobility, anti-radiation and heat bearing capabilities and it has not been given much attention in the past to use as substrate for the growth of InAlN films. Furthermore, growth of InAlN film on sapphire and glass has been investigated to make a comparison of In-rich InAlN film properties on different substrates. The InAlN films with optimized properties on Si (111) and GaAs (100) have been employed for the photodetectors application.

1.4 Objectives of Research

This present work focuses on the growth of InAlN films by using reactive magnetron co-sputtering technique and confers upon the structural, surface and electrical properties of these films. The main objectives of the present work are as follows;

1) To grow InAlN films with different In and Al mole fractions on p-type Si (111) substrates by using reactive magnetron co-sputtering technique and to investigate the effects of changing composition on the structural, surface and electrical properties of these films.
2) To optimize the deposition conditions such as substrate temperature, film thickness and gas flow ratio for In-rich InAlN film grown on Si (111) substrates.
3) To study the growth and characteristics of In-rich InAlN films on different substrates such as Si, sapphire, glass and GaAs under similar deposition conditions.
4) To investigate the growth of InAlN films on GaAs (100) substrates in a wide composition range that has not been given attention before.
5) To fabricate and characterize InAlN based photodetectors on Si (111) and GaAs (100) substrates.

1.5 Scope of Study

The scope of this study lies in preparing In-rich InAlN film on Si (111) by using reactive magnetron co-sputtering technique under various depositions conditions and to investigate its structural, surface and electrical properties. The growth conditions for InAlN films on Si (111) substrates have been optimized by varying the film composition, substrate temperature, gas flow ratio and the film thickness. A comparative study on InAlN films growth on different substrates has been made under similar deposition conditions. Furthermore, growth of InAlN film on GaAs (100) substrates has also been investigated at different sputtering powers of Al that has not been given much attention before. Finally, the films grown on Si (111) and GaAs (100) have been employed to fabricate InAlN based photodetectors.

1.6 Originality of Thesis

Since there is a lack of information on the growth of In-rich InAlN films due to low dissociation temperature of InN as well as due to lack of a suitable substrate, therefore, in this work, an attempt is made to grow In-rich InAlN films using low temperature reactive magnetron co-sputtering technique on different substrates. In particular, growth of magnetron sputtered InAlN films on Si (111) has been studied in detail and suitable deposition conditions for the growth of InAlN on p-Si (111) have been explored for the first time. A comparison between different properties of InAlN films grown on different substrates has been made under the similar growth conditions that has been lacking in the previous studies. The Si (111) substrate has been chosen because of its lowest lattice mismatch with In-rich InAlN films as compared to the other substrates and it is also a low cost and commonly available substrate. In addition to this, growth of InAlN films on GaAs substrates has been studied that was not given much attention before. The prepared InAlN films on Si (111) and GaAs (100) have been used to fabricate InAlN based photodetectors.

1.7 Organization of Thesis

Chapter 1 of this thesis deals with the introduction to III-V nitrides and objectives of the present research work. This chapter presents an overview of InAlN films and highlights the existing problems in the synthesis of these films. Furthermore, objectives of the research work and scope of the present study are described in this chapter.

Chapter 2 contains a brief literature review about growth, properties and applications of InN, AlN and InAlN films. It also deals with the theory related to magnetron sputter deposition technique along with description about metal-semiconductor contacts. In the beginning of chapter 2, an overview of literature on InN and AlN is presented which is followed by a description about the research work carried out to synthesize InAlN alloys using various techniques. The properties and applications of InAlN films are also highlighted. A comprehensive literature survey about InAlN films has been made using different growth techniques. This is followed by a detailed description about the fundamentals of magnetron sputtering deposition, metal-semiconductor contacts and photodiodes.

Chapter 3 contains experimental procedure and various characterization tools. The characterizations used in this work have been described in detail in chapter 3.

Chapter 4 contains the results and discussion on the growth and characterizations of InAlN films on Si (111) substrates. In the first section of this chapter, effects of In mole fraction on the structural, surface and electrical properties of InAlN films have been studied. Furthermore band gap of InAlN films has also been evaluated at different film compositions. In the second section, growth and characterization of InAlN films have been made at different substrate temperatures. In the third section of this chapter, InAlN film growth and properties have been studied at different film thicknesses. In the fourth and final portion of the chapter, effects of Ar:N_2 gas flow ratios on the growth and properties of InAlN films have been described. The structural, surface and electrical properties of InAlN films have been studied at different values of Ar:N_2 gas ratios. In general this chapter provides comprehensive information about InAlN films growth on Si (111) substrates.

Chapter 5 deals with the study of In-rich InAlN films growth on different substrates. A comparative study on the films growth and properties has been made on Si (111), c-plane sapphire, GaAs (100) and glass substrates under similar deposition conditions. The structural, surface and electrical properties of these films have been highlighted. The band gap of the films on different substrates has also been evaluated. In addition to this, growth of InAlN films on GaAs substrates has been studied at different Al powers. The structural, surface, electrical and optical properties of the grown films have been discussed.

Chapter 6 deals with the characterization of InAlN based photodetectors. In the first part, InAlN/Si(111) based MSM photodetector has been characterized. The second part of this chapter contains the characterization of n-InAlN/p-Si(111) based p-n heterojunction photodiode. The third and final part describes the characterizations of InAlN/GaAs(100) based MSM photodector. The parameters such as dark current, photocurrent, current gain, sensitivity, responsivity and response/recovery time of the fabricated devices have been discussed.

Chapter 7 deals with the conclusions obtained from the present work. The results obtained have been summarized in this chapter.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 Introduction

This chapter presents a brief review about the growth and properties of InAlN films. It also describes fundamentals relating to magnetron sputtering deposition and theory of metal-semiconductor-metal contacts. The techniques used for the growth of InAlN films in the past are discussed in this chapter. Furthermore, difficulties associated with the growth of InAlN films are also highlighted. Since InAlN is an alloy of InN and AlN, therefore, before discussing about InAlN films, a short review about the growth history and fundamental properties of InN and AlN has been presented. This chapter is divided into three parts. The first part contains an overview of InN and AlN growth and properties, the second part consists of the literature review on the growth and properties of InAlN alloys whereas third and final part describes the fundamentals of magnetron sputtering technique, metal-semiconductor-metal contacts and photodetectors.

2.2 Overview of InN Growth

Indium nitride (InN) is a promising group III-V nitride that has gained a considerable interest among researchers in the past due its remarkable inherent properties such as narrow band gap (0.7 eV), smallest effective mass, high electron mobility and high drift velocity. Therefore, it finds potential applications in optoelectronics and high speed electronic devices [33-34]. As compared to AlN and GaN, InN has been the least studied material owing to difficulties associated with its low dissociation temperature and high equilibrium pressure of nitrogen over InN [2].

The first ever attempt to grow InN was made by Juza and Hahn in 1938 when the wurtzite InN was synthesized from $InF_6(NH_4)_3$ [35]. Afterwards, further attempts were made by different groups of researchers to synthesize InN by using various chemical techniques [36-37], however, growth of high quality InN was not successful because of the difficulties in direct interaction of indium with nitrogen in an activated form [38]. The success in the growth of InN with slightly better crystalline quality was achieved by Hovel and Cuomo in 1972 when they were able to synthesize polycrystalline InN films on silicon and sapphire substrates using radiofrequency (RF) sputtering technique in the temperature range 25 ^{o}C to 600 ^{o}C. However, these films contained high electron concentrations and low electron mobility [39]. In 1980's, more works were carried out to grow good quality InN by various researchers mainly through RF sputtering [40-44]. Although some improvements were made to obtain InN with better physical properties, however, many properties of good quality InN remained unclear in these studies.

The first epitaxial growth of InN was first successfully done in 1990 by Matsuoka and other researchers by using metalorganic chemical vapor deposition (MOCVD) technique on the sapphire substrates [45]. This opened a new door for the epitaxial growth of InN film to improve its structural, optical and electronic properties. The epitaxial growth of InN films was further studied in 1990's onward by various groups using MOCVD and molecular beam epitaxy (MBE) techniques on different substrates under different growth conditions [46-49]. It has been found that the synthesis of InN using high temperatures epitaxial techniques may involve thermal decomposition of InN which affects its crystalline quality [50-51], therefore, low temperature growth techniques such as magnetron sputtering was also employed. Initial work on the growth of InN using reactive magnetron sputtering revealed the formation of polycrystalline InN films with low structural quality due to defects in the films. These defects were thought to be responsible for increasing the band gap of InN [52]. Later on, after year 2000, a number of studies were carried out to improve the structural quality of magnetron sputtered InN film [53-56]. The previous literatures reveal that the InN films using magnetron sputtering can be synthesized even at room temperature [55-56]. In addition to MOCVD, MBE and magnetron sputtering technique, some other techniques such as atomic layer deposition and reactive evaporation were also used to synthesize InN [57-58]. However, the crystalline quality of InN grown by using these techniques was found to be lower as compared to MOCVD and MBE techniques. By going through the literature survey on InN, it is clear that the low dissociation temperature and choice of a suitable substrate restricts the growth of high quality InN films. Therefore, efforts are still in progress to improve the growth conditions and crystalline quality of InN films.

2.3 Overview of AlN Growth

Aluminum nitride (AlN) is a wide band gap semiconductor material whose band gap is 6.2 eV. It has been focus of research in the past because of its remarkable properties that make it useful for many optoelectronic applications. It possesses high thermal conductivity, low thermal expansion coefficient, high refractive index, high breakdown dielectric strength and high acoustic wave velocity. Furthermore, high thermal and chemical stability of AlN makes it a suitable material for applications in high temperature environments. Owing to these remarkable applications, AlN finds applications in electronic packaging, electronic structures and for piezoelectric and acoustic devices [59-62].

The AlN was first synthesized in 1877, however, growth of AlN with high crystal quality was not successful until 1980’s. The epitaxial growth of AlN with high crystalline quality after 1990’s opened a new door for the realization of its potential applications in microelectronics due to its high thermal conductivity [63]. Various techniques such as chemical vapor deposition (CVD) [63], MBE [64], pulsed laser deposition (PLD) [65], and magnetron sputtering [66-68] were used to grow AlN films on various substrates. The CVD technique has been the most commonly used technique to grow AlN in the past. In most of the studies carried out by using CVD, growth temperature above 973 K was used to improve the crystalline quality of AlN films [63, 69]. Despite the success of obtaining epitaxial AlN films using CVD, AlN films with smooth surfaces could not be obtained using this technique. Auner *et al.* [64] synthesized AlN films on Si (111) substrates between 400 ^{o}C to 600 ^{o}C by using plasma source MBE. It was observed that the AlN films grown at 400 ^{o}C form initial amorphous region whereas the amorphous region is considerably reduced at 600 ^{o}C. In addition to CVD and MBE, AlN films synthesized using PLD indicated that the growth quality of AlN can be improved by improving the growth conditions and nitrogen supply during the film deposition [65]. The RF magnetron sputtering is another useful low temperature growth method which is much economical as compared to the CVD and MBE techniques. The growth of AlN films using reactive sputtering on different substrates has also been extensively investigated in the past [66-70]. The survey of literature reveals that the growth of AlN with improved crystalline quality has been achieved and AlN films are much easier to grow as compared to the InN films.

2.4 Fundamental Properties of InN and AlN

InN possesses hexagonal wurtzite structure which is more stable than the cubic zinc-blende structure, therefore, InN is mostly formed in wurtzite structure. The lattice parameters a and c of InN have been reported to be a = 3.53 Å and c= 5.70 Å [42]. InN is generally believed to be of n-type nature with high background carrier concentration (~ 10^{19} cm^{-3}) [52]. The high background carrier concentration is due to the defects generated in the material during its growth. The value of background carrier concentration depends upon the type of technique used to grow InN films. In the case of RF sputtered InN films, the value of background carrier concentration has been found to be much larger as compared to the background carrier concentration in the films grown using the epitaxial technique such as MBE or MOCVD [44]. The thermal conductivity value of InN is quite low. A typical value of thermal conductivity of InN in literature has been found to be 0.45 $Wcm^{-1}K^{-1}$. The band gap energy of InN in initial studies was found to be 1.9 eV, however, in 2002, growth of InN using the epitaxial techniques revealed its narrow band gap of 0.7 eV [71]. The revision of band gap of InN from 1.9 eV to 0.7 eV opened a new door for its use in the electronic and optoelectronic applications.

The AlN also possesses wurtzite hexagonal structure with lattice constants a = 3.112 Å, c = 4.982 Å [69]. In this structure, each Al atom is surrounded by four N atoms, forming a distorted tetrahedron with three Al-N bonds. The structural properties of AlN are characterized through its structural orientation. For the AlN films to be useful as a piezoelectric material in miroelectromechanical systems (MEMS) and surface acoustic wave (SAW) devices, the resistivity of these c-axis oriented films must also be high. The carrier concentration value in AlN has been found to be quite low and electrical resistivity is quite high as compared to that of the InN. The typical carrier concentration found in AlN films is ~ 10^{6} cm^{-3}. The thermal conductivity of AlN has been found to be quite high as compared to the InN. The thermal conductivity value of AlN found in the literature is 245 $Wcm^{-1}K^{-1}$. The band gap of AlN has been found to be quite large as compared to the band gap of the InN. The band gap value of AlN in the literature is accepted to be 6.2 eV [72].

2.5 Overview of InAlN Growth

The first ever attempt to grow InAlN film was carried out by Starosta by using RF magnetron sputtering in 1981 [73]. The films were grown on glass substrates at 400 ^{o}C using reactive multi-target sputtering which caused the formation of polycrystalline films. In 1989, Kubota and co-workers reported an improvement in the crystalline quality of the Al-rich InAlN films on sapphire substrates by incorporating AlN buffer layer on the substrates [74]. The first ever attempt to grow InAlN film using MOCVD was made by Guo *et al.* in 1995 [75]. The InAlN films were prepared on c-plane sapphire substrates at 600 ^{o}C. These were found to be n-type single crystalline films having large electron concentration ~10^{20} cm^{-3}. This work was followed by the growth of $In_{0.16}Al_{0.84}N$ film on GaAs substrates using MBE technique [76]. However, despite the epitaxial growth by using MOCVD and MBE techniques, these films were found to contain a large number of defects and high electron concentration. During the period of 1997 to 2000, more studies were conducted to prepare InAlN films on GaN substrates [5-8]. These studies revealed that InAlN film having 83 % of indium contents shows prefect lattice matching to GaN and therefore a high structural quality film can be obtained on the GaN substrates [24, 77-78]. The revision of narrow band gap of InN in 2002 opened a new door for researchers to also grow $In_xAl_{1-x}N$ films in the indium-rich region. Therefore, onwards from the year 2002, a number of studies were carried out to prepare these films mainly by using MOVPE and MBE techniques, however, due to low dissociation temperature of InN, success could not be achieved to a great deal.

This section presents a review on the growth kinetics, properties and applications of $In_xAl_{1-x}N$ films prepared on different substrates. Growth of these films carried out using MOCVD, MBE and RF/DC magnetron sputtering in the past has been briefly described here. The difficulties and challenges in synthesizing $In_xAl_{1-x}N$ films are highlighted. Effects of In and Al contents, buffer layer incorporation, substrate nature, growth temperature, pressure and V/III gas ratio have been discussed in detail. An overview of the structural, surface, optical and electrical properties of these films has also been presented here.

2.5.1 Growth Techniques

InAlN films on different substrates have been grown by using MOCVD, MBE and reactive magnetron sputtering techniques. The details of InAlN films growth using these techniques are described as follows;

2.5.1 (a) Metalorganic Chemical Vapor Deposition

Metalorganic chemical vapor deposition (MOCVD) is one of the commonly used techniques for the synthesis of group III-V nitrides. It is also known as metalorganic vapor phase epitaxy (MOVPE). This technique is used to deposit thin layers of atoms on a semiconductor wafer. Using this technique several layers can be built up on a wafer with precise control of thickness. As the MOCVD names implies that it uses metal organic compounds as precursors which usually consists of an organic trimethyl (TM) or triethyl (TI) group connected to group-III metals such as In, Al, or Ga. The group-V precursors are used in the form of hydrides such as AsH_3 (arsine) or NH_3 (ammonia). The advantages of MOCVD includes faster growth rate, achievement of multi-wafer capability, higher growth temperature, growth process is thermodynamically favorable and better layer quality than the other techniques. However, there are some disadvantages of this technique which are related to the use of toxic gasses in MOCVD process and difficulties to monitor the growth rate, gas flow issues etc.

A number of efforts have been made to synthesize InAlN films by using

MOCVD technique. The literature shows that the growth conditions such as V/III ratio, growth temperature and gas pressure play an important role in controlling the film crystalline quality [79-82]. Sakai *et al.* [79] studied the effects of V/III gas ratio on InAlN/GaN films grown by MOCVD in the temperature range 740^{o}C-840 ^{o}C. It was noticed that a decrease in V/III gas ratio results in the formation of a good quality InAlN film. On the other hand, Kang and co-workers [30] reported an increase in the crystallinity of InAlN films by increasing the V/III gas ratio, which was attributed to an increase in aluminum incorporation inside the films. However, an increase of aluminum contents resulted in a phase separation in the films.

Chung and co-workers [80] investigated the effects of growth parameters such as gas pressure (70-300 torr), V/III ratio (10000-19000), growth rate (80-240 nm/h) and carrier gas ratio (0 to 0.2) on the MOCVD grown $In_xAl_{1-x}N$ films ($0.76<x<0.86$) on GaN template. The indium composition in the film was found to increase with increase of the gas flow ratio whereas the low growth temperature and high growth pressure lead to an increase in the carbon incorporation in the films. Similarly, Chauveau *et al.* [81] studied the growth of Al-rich $In_xAl_{1-x}N$ ($x\leq0.2$) epilayers on GaN/sapphire substrates using MOCVD. The indium incorporation in the films was increased with increase of the gas pressure; however, the high gas pressure resulted in a decrease of the film crystalline quality. The surface morphology indicated a reduction in the V-shaped defects with decrease of the ammonia flow rate. However, the size of V-shaped pits present in the film was increased with increase of the film thickness. The results of this work suggested that by controlling the amount of V-types defects, the crystallinity of InAlN film can be enhanced.

Liu *et al.* [82] studied effects of growth temperature, pressure and V/III ratio on growth, indium contents and surface morphology of MOVPE grown InAlN films. It was observed that by decreasing growth temperature from 850 ^oC to 750 ^oC, indium contents in InAlN alloys are increased from 0.37 % to 21.4 %, whereas, by increasing the pressure from 20 torr to 100 torr, the indium concentration in the film is increased from 16 % to 25 %. The low gas pressure and higher V/III ratio helped in improving the surface morphology of the films.

Thermal stability of InAlN film has also received a considerable importance because of low dissociation temperature of InN. Gadanecz *et al.* investigated the thermal stability of MOCVD grown InAlN films on GaN/Si (111) substrates [29]. The films were given heat treatment at temperature ranged 30 ^oC to 960 ^oC. The samples with indium contents 17 % showed long stability even at high temperature (960 ^oC). In another study, Yu *et al.* [84] investigated the thermal stability of InAlN and AlGaN barriers high electron mobility transistor (HEMT) structures after their post-deposition annealing at 800 ^oC. They found that the $In_{0.17}Al_{0.83}N$ barrier HEMT structures show less stability in their electrical properties as compared to the $Al_{0.3}Ga_{0.7}N$ structures. Recently, it has been found that the InAlN/GaN hetrostructures capped with a thin GaN layer show high thermal stability even after annealing at temperature above 800 ^oC [85].

By going through the literature survey regarding MOCVD growth of InAlN alloys, it is clear that by controlling the growth conditions such as growth temperature, V/III gas ratio and gas pressure, the crystalline quality of these alloys can be controlled. However, MOCVD growth suffers from the problem of phase separation and dissociation of indium nitride at high temperatures.

2.5.1 (b) Molecular Beam Epitaxy

Molecular beam epitaxy (MBE) is another useful technique to deposit nitride films on different substrates. The term epitaxy is derived from the Greek word “epi” means above and taxis means in ordered form. Therefore, the epitaxy term is related to the growth of thin film layer by layer. In MBE, the elemental source materials such as In, Ga, Al and N are evaporated on a heated substrate in ultrahigh vacuum ($\sim 10^{-9}$ Torr) to produce thin films. By monitoring and controlling the behavior of reactants from solid precursors, the structural and electrical quality of III-V nitride materials can be improved. The MBE has an advantage of higher deposition rate as compared to the MOCVD that allows the films to grow epitaxially [86].

A number of efforts have also been made to use MBE technique for InAlN films growth. Following the first attempt made by Aberthnay *et al.* [76] in 1995, a series of studies were conducted to grow InAlN films by using MBE technique [25, 87-92]. Terashima *et al.* [25] studied the growth of InAlN films in a whole composition range on GaN template at different temperatures ranging from 500 ^{o}C to 600 ^{o}C by using MBE. They observed that the film shows good structural and optical properties till 580 ^{o}C, however by increasing the growth temperature to 600 ^{o}C, the crystalline quality of the film was deteriorated. Iwata and co-workers [87] reported that indium composition in the MBE grown InAlN alloys can be controlled by controlling the indium flux. On the other hand, Uddin *et al.* [88] showed that the growth temperature plays an important role in controlling the indium composition in the films. They investigated the effects of growth temperature on the indium incorporation inside InAlN grown using MBE in the temperature range 580 ^{o}C to 360 ^{o}C. The Al-rich InAlN alloys were grown on Si (111) substrates in the presence of an AlN buffer layer using gas source MBE. The film composition was varied by varying the growth temperature from 580 ^{o}C to 660 ^{o}C. It was observed that compositional uniformity can be achieved at 580 ^{o}C. However, by increasing the temperature beyond this, the growth rate and indium incorporation in the films are considerably decreased. Zhou and co-workers [89] observed lateral phase separation in InAlN/GaN heterostructures grown by plasma assisted MBE. This phase separation was attributed to the random compositional fluctuations during the early stages of the growth due to misfit strain relaxation. Wu *et al.* [90] have studied the growth of In-rich InAlN film on GaN/sapphire substrates using MBE technique. The results of these experiments showed that the InAlN film with 85 % indium contents can be grown without phase separation. Chen *et al.* [91] reported the effects of growth temperatures on the crystalline quality of InAlN film prepared using MBE technique in the temperature range 460 ^{o}C to 540 ^{o}C on silicon substrates. The films grown were found to be of single phase and oriented towards (002) plane. The high resolution transmission electron microscope (HR-TEM) results indicated that InAlN films can be directly grown on silicon at 460 ^{o}C without any interfacial reactions. Recently, Chowdhury *et al.* [92] have demonstrated that the structural quality of Al-rich $In_{0.17}Al_{0.83}$/GaN heterostructures grown on silicon substrates using MBE technique is improved by improving the thickness of the buffer layer.

2.5.1 (c) Reactive Magnetron Sputtering

Reactive magnetron sputtering is a low temperature growth method that has drawn tremendous attention of researchers to grow semiconductor thin films in the past. It is a useful physical vapor deposition technique that can be effectively used to deposit high quality thin films on a large area of substrates at low cost. Keeping in view the difficulties associated with high temperature growth of InAlN films using MOCVD and MBE techniques, the low temperature growth method such as RF/DC magnetron sputtering is gaining an increasing importance in recent years. The advantage of this method over MOCVD and MBE is that the InAlN films can be grown at much lower temperatures using this technique without any phase separation.

In the past, various efforts have been made to grow InAlN films by using magnetron sputtering technique. Following the earlier studies by Starosta [73] and Kubota [74], further attempts were made by different groups of researchers to use reactive magnetron sputtering technique to synthesize InAlN films on different substrates in late 1990s and onward from the year 2000. Peng *et al.* [93] synthesized InAlN film on silicon, glass and quartz substrates at 200 ^{o}C by using reactive DC and RF magnetron sputtering of pure Al and In targets respectively. They found the existence of InAlN diffraction peaks at (002), (102) and (103) planes respectively. Guo *et al.* employed RF magnetron sputtering to synthesize InAlN films on sapphire substrates at 100 ^{o}C [94]. The films obtained were found to be c-axis oriented and composition of the films was controlled by changing the ratio of sputtered area of aluminum plate to the indium plate. However, in their later studies, it was found that the composition and band gap energy of InAlN films grown on glass and sapphire substrates using reactive RF magnetron sputtering can be controlled by varying the RF power [95-96].

The literature reveals that an addition of a suitable buffer layer on a substrate can improve the structural quality of these films [74]. The presence of buffer layer whose lattice constant is close to the lattice constant of InAlN greatly reduces the defects between the film and the substrate thereby increases the structural quality of film. In this regard, a number of studies reported that with use of AlN, GaN, TiN and ZrN buffer layers on different substrates, the crystalline quality of these films was improved [97-101]. Seppanen and coworkers [97] found that the presence of TiN and ZrN buffer layers on sapphire substrate improves the crystalline quality of InAlN films. InAlN films were prepared on TiN and ZrN seed layers at different temperatures (300^{o}C-900^{o}C) using RF magnetron sputtering technique. The crystalline quality of the films was found to change with changes in deposition temperatures and with choice of the seed layers. Dong *et al.* [98] prepared (002) oriented Al-rich InAlN film on glass and sapphire substrates with AlN buffer layer at 300 ^{o}C by using reactive magnetron sputtering system. The structural and surface analyses of these films indicated that the films formed on sapphire showed better crystallinity as compared to the films prepared on glass. The better crystallinity on sapphire shows lesser structural defects inside the film as compared to the film grown on the glass. This resulted in lower electrical resisitivty of InAlN film on the sapphire than on the glass substrate. Tung and co-workers [99] studied the synthesis of InAlN films on glass substrates by pulsed DC reactive sputtering at 200 ^{o}C to 400 ^{o}C. The results indicated that crystallinity of the thin films increases with increase of substrate temperature and with incorporation of AlN seed layer on the glass substrates. Similarly, Han *et al.* [100] used reactive magnetron sputtering technique to synthesize $In_xAl_{1-x}N$ films on AlN/sapphire substrates with variable composition x. The grain size of the film was found to increase with increase in the x value. The electrical resisitivty was decreased with increase of the In composition x. In a recent study, Besleaga *et al.* [102] used reactive RF magnetron co-sputtering technique to grow $In_xAl_{1-x}N$ thin films on glass and polyethylene terephthalate substrates. XRD measurements revealed a (002) oriented preferential growth of InAlN films, however, by increasing the x value to 0.5, the preferential orientation of the film was shifted towards (101) plane. In another recent study, Alizadeh *et al.* [103] used plasma-assisted dual source reactive evaporation technique to grow $In_xAl_{1-x}N$ films (with composition x ranging from 0.3 to 0.4) on the quartz substrates. the films grown were found to be amorphous with low structural intensity.

The survey of literature reveals that only limited studies have been carried out on the growth of InAlN films by using different techniques. In most of the studies, sapphire and glass substrates have been used for the growth of Al-rich InAlN films whereas the data regarding the growth of In-rich films on silicon and GaAs substrates using magnetron sputtering technique is quite limited [104]. Silicon is commonly available low cost material that can be potentially used for the growth of InAlN films [101]. Among different types of silicon substrates, the Si (111) possess lowest lattice mismatch with the InN film [105], therefore, it can be potentially used to grow In-rich InAlN films. On the other hand, the reactive magnetron sputtering is a low cost and low temperature growth method as compared to the epitaxial techniques such as MOCVD and MBE, therefore, it can be effectively employed for the growth of In-rich InAlN films without any phase separation. Therefore in the present work a particular attention has been paid to grow In-rich InAlN films on Si (111) substrates and structural, surface and electrical properties of these films were studied.

2.6 Physical Properties of InAlN

2.6.1 Structural Properties

The structural properties of InAlN films play an important role in controlling the other physical properties of these films such as the surface, optical and electrical properties for their efficient use in the optoelectronic devices. However, obtaining InAlN alloy with good structural quality is found to be quite hard because of the large differences in the lattice parameters of InN and AlN. Furthermore, the low dissociation temperature of InN makes it quite difficult to prepare these alloys at high